

XI. *On Spontaneous Nitrification.* By C. F. SCHOENBEIN, *Professor of Chemistry in the University of Bâle.* Communicated by MICHAEL FARADAY, *Esq., F.R.S., &c.*

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A FACT not yet well understood is the spontaneous formation of nitric acid, or rather nitrates which takes place when azotic organic matters putrify in contact with strong bases and atmospheric air. Some chemists hold the opinion that under the circumstances mentioned, nitric acid is formed out of the nitrogen of the organic substances and atmospheric oxygen, both elements being determined to unite with one another by what is called the predisposing affinity of the bases for nitric acid.

Others maintain that the said acid originates entirely from the oxygen and nitrogen of the atmosphere, and suppose that these elements are by a sort of capillary action brought into such a condensed state as to combine into nitric acid, under the additional influence of the predisposing affinity of the bases for that acid.

According to the notions prevailing at present nitric acid comes from ammonia, which is supposed to be acted upon by the oxygen of the air, *i. e.* dehydrogenized, and its nitrogen united to oxygen. The only thing sure is, that we know very little about spontaneous nitrification.

Considering the theoretical interest connected with the obscure phenomenon in question, it must appear very desirable that novel facts should be ascertained calculated to throw light upon, and lead to the true insight into, the cause of spontaneous nitrification. The observations I am about to state will perhaps contribute a little to obtain that end.

Some years ago I ascertained the fact, that a solution of potash, sufficiently long treated with air ozonized (by the means of phosphorus), yields a liquid which, being over-saturated with sulphuric acid and heated, causes a brownish coloration round a crystal of sulphate of iron, and has the power of destroying indigo*. From that fact I inferred at the time that the reactions indicated are due to the presence of a nitrate.

Some time after I found out that the acid liquid called phosphatic acid, produced during the action of phosphorus upon moist atmospheric air, enjoys likewise the property of destroying indigo. If that acid is perceptibly coloured by a solution of indigo and left to itself, after a few hours it will have become colourless, or if the same acid be heated, its colour will be discharged within a few minutes.

Phosphatic acid, some iodide of potassium being dissolved in it, assumes a yellowish

* See Les Archives de l'Electricité, No. 15, p. 417.

brown colour, and the same acid being neutralized by hydrate of lime, yields in small quantities a salt exhibiting all the properties of nitrate of lime. The latter being treated, for instance, with carbonate of ammonia, produces a salt which, when mixed with some strong sulphuric acid and brucine, strikes a blood-red colour, disengages fumes of hyponitric acid, &c. From these facts it appears that nitric acid is present in the phosphatic acid, the former being produced during the oxidation which phosphorus undergoes in moist atmospheric air.

I have further ascertained that hydrate of lime, being suspended in water and sufficiently long treated with ozonized air, produces a salt exhibiting the properties of a nitrate.

M. FELLEBERG has published* results which lead also to the conclusion, that either nitrites or nitrates are formed in treating hydrate of lime with ozonized atmospheric air, and the same chemist has made observations with the phosphatic acid coinciding with the results I have obtained from my own experiments. The philosopher of Lausanne is rather inclined to identify ozone with hyponitric acid. I think, however, that such an opinion cannot be upheld, and is contrary to facts, of which I gave an account in POGGENDORFF's Annals some time ago. According to my experiments, ozone destroys instantaneously hyponitric acid, hydrate of nitric acid being formed. Phosphorus does not shine in atmospheric air containing the smallest quantity of hyponitric acid, whilst phosphorus exhibits a very lively disengagement of light when placed in atmospheric air, being ever so strongly charged with ozone. Blue litmus paper being suspended in air of the latter description is not in the least reddened, but simply and rapidly bleached; whilst the same paper placed in atmospheric air, which is only slightly charged with hyponitric acid, assumes a perceptibly red colour. Ozonized air being charged with vapour of ammonia or carbonate of ammonia so strongly as to bring back instantly the blue colour of reddened litmus paper, enjoys the property of decomposing iodide of potassium (*i. e.* colouring blue the parts of starch mixed with that iodide), transforming the yellow prussiate into the red salt, colouring blue the resin of guaiacum, destroying all organic colouring matters, changing sulphuret of lead into a sulphate, &c.: the facts stated are sufficient to prove satisfactorily that ozone is not identical with hyponitric acids. I have, however, some other facts to mention which will demonstrate in the most direct manner, that ozone has nothing to do with the acid mentioned.

Ozone is abundantly produced (by means of phosphorus) in moist mixture of perfectly pure oxygen and hydrogen, or oxygen and carbonic acid. Ozone is generated by electrical sparks out of the purest oxygen obtainable, provided that principle contain some moisture. Ozone makes its appearance round the positive electrode, if a current passes through acidulated water containing no trace of nitrogen or any azotic compound. We are therefore allowed to consider it as a settled matter, that ozone is different both from nitrous and hyponitric acids.

* See Les Archives de l'Electricité, No. 17, p. 24-34.

Now, if a nitrate happens to be formed in treating, for instance, hydrate of lime with ozonized atmospheric air, it seems to follow that the nitric acid formed under those circumstances, owes, in some way or other, its origin to ozone, pure atmospheric air being unable to produce a nitrate with the hydrate named. But in what manner does ozone contribute to the formation of that acid? My experiments have shown that ozone is a very powerful oxidizing agent, so much so, that even iodine and silver are at the common temperature transformed into iodic acid and peroxide of silver. If it be a fact that the chemical powers of the oxygen contained in ozone are so much exalted as to enable that oxygen to unite with substances so little oxidable as iodine and silver are, it would not appear in my eyes very surprising if that same oxygen should happen to combine, under certain circumstances, with nitrogen to form what is called nitric acids.

According to my opinion (see my little work on the Slow and Rapid Combustion of Bodies) there does not exist a compound of nitrogen = NO_5 . I consider what chemists call the first hydrate of nitric acid as $\text{NO}_4 + \text{HO}_2$, and the normal nitrates as $\text{NO}_4 + \text{RO}_2$. Nitrate of lime is therefore to me $\text{NO}_4 + \text{CaO}_2$. Agreeable to that view, I am inclined to account for the nitrification above mentioned in the following manner. Ozone transforms first CaO into CaO_2 , a change which, according to my recent experiments, a number of basic oxides undergo within an ozonized atmosphere. The oxides of manganese, lead, cobalt, nickel, and silver, for instance, are readily transformed by ozone into their corresponding peroxides. Whilst peroxide of calcium is formed, ozone exerts an oxidizing influence also upon the nitrogen contained in atmospheric air, and forms NO_4 , which uniting to CaO_2 , produces what we call nitrate of lime.

The fact, that electrical sparks passing through a moist mixture of oxygen and nitrogen generate nitric acid, was first ascertained by CAVENDISH, 1785; in 1840 I made the observation that under the same circumstances ozone is produced. DAVY has found that traces of nitric acid are formed around the positive electrode if a current passes through water containing atmospheric air or nitrogen, and I have ascertained that under the same circumstances ozone is generated.

From the facts above stated, it appears that during the slow combustion which phosphorus undergoes in moist atmospheric air nitric acid is formed, and we are now well aware that ozone makes its appearance at the same time. The invariable concomitance of the two phenomena mentioned, *i. e.* the contemporary formation of nitric acid and ozone which takes place under circumstances apparently so very different from each other, gives room to suspect that the production of one of those compounds is in some way or other connected with the generation of the other.

As electrical sparks are able to produce ozone out of moist and otherwise pure oxygen, it appears that the formation of that substance is entirely independent of the generation of nitric acid, and it becomes highly probable that the ozone produced, under electrical influence, out of moist atmospheric air has nothing to do with the

nitrogen of the atmosphere. Now if ozone be capable of forming nitrate of lime by being treated both with nitrogen and hydrate of lime, it is very possible that ozone coming in the very moment of its formation in contact with nitrogen and water, produces what is called hydrate of nitric acid. Nitrogen being oxidized by ozone into NO_4 , this compound would unite with an equivalent of HO_2 (ozone) and form hydrated nitric acids.

According to that view, the nitric acid generated,—

1. On electrifying moist atmospheric air ;
 2. On electrolysing water containing nitrogen, *i. e.* air ;
 3. On making phosphorus to act upon a moist mixture of oxygen and nitrogen ;
- would be formed in a secondary way, that is to say, in consequence of the oxidizing effects produced by ozone upon nitrogen.

Supposing the suspected connexion really exists between the formation of ozone and the generation of nitric acid, we can easily understand the concomitant appearance of both, and conceive that where ozone is produced, nitric acid also must be formed, provided there be nitrogen and water present at the spot where ozone happens to be generated. If, agreeably to the views hitherto developed, the nitric acid formed on electrifying moist atmospheric air ; electrolysing water charged with some azote ; or making phosphorus to act on a moist mixture of oxygen and nitrogen, owes its origin to the ozone being produced under those circumstances, what is the cause of the generation of that acid which is formed during the putrefaction of azotic substances being in contact with strong bases and air ? The putrefaction of those substances consisting, as it is well known, partly at least, in an act of oxidation or slow combustion of their oxidable constituent parts, and it being a fact that during the slow combustion of phosphorus, vapour of ether, or alcohol in atmospheric air, a highly oxidizing agent (ozone) makes its appearance, we may be allowed to compare the slow combustion of phosphorus with the putrefaction of azotic organic matters, both of them taking place in the atmosphere. And if it be a fact that during the slow combustion of phosphorus and ether, ozone is produced, it does not seem to be an over-bold conjecture to suppose that ozone is also formed during the putrefaction of azotic substances, and the nitrogen of those matters oxidized into nitric acid. As phosphorus which contains no trace of nitrogen, nevertheless forms nitric acid on its being slowly burned in atmospheric air, it seems to be not impossible that organic substances containing no nitrogen produce also ozone, and along with it nitric acid during the slow oxidation they undergo in atmospheric air. It seems to me to be important to ascertain, by accurate experiments, whether, under the circumstances last mentioned, nitric acid or nitrates are formed. Some observations made by BRACONNOT and SAUSSURE seem to speak in favour of such a formation, they are however too vague to decide the question. To arrive at certainty regarding that fact is important, not only with respect to the theory of spontaneous nitrification, but also with reference to a matter which has of late been the subject of much discussion.

From what source does the vegetable world draw the nitrogen which we meet in so many of her products? If, according to a prevailing notion, it be only nitrogen in a compound state that can be assimilated by plants, is it not possible that nitrogen contained in nitrates might be as well taken up by them as the azote of ammonia? It is easy to see that in the affirmative case some nitrogen would be offered to growing plants by the means of organic substances containing no azote, and putrefying in the atmosphere. I do not intend, however, to meddle with those transcendent questions of physiological chemistry, and leave the answering of them to those who are much better qualified than myself to solve problems of such an intricate and difficult nature.

Bâle, October 1845.